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Title of the article

MODELLING OF METAL POLLUTANT LEACHING THROUGH A SMECTITE

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Abstract

Laboratory tests are performed to characterise the soaking and retention properties of a clay barrier (Fo-Ca) under controlled homogeneous conditions. A physical model that allows calculating the retention properties and kinetics observed during the test is then detailed, and lastly simulations are examined using various soaking conditions. The results show the model predictions of cumulative cation concentrations in leachates (i.e. copper retention by clay). These curves are accurately fit by the model with the experimental data for the leaching phenomena. Clay retention capacity until reaching a physical limit in the exchanges is evidenced as well, with this limit being input into the model as the clay CEC.

Keywords

Leaching; metals; clay; copper; kinetic; modelling; CEC

1. Introduction

In pursuit of sustainable development goals for the benefit of future generations, it is important to preserve the quality of water resources in order to protect human health. While humanity faces the challenge of increased waste production (OECD, 1997) across all countries, the techniques for eventually confining waste vary throughout the world. The multi-barrier system has been adopted in several countries, and this includes the use of natural or geosynthetic clay liners at the bottom of landfills. In the European Union, a geological barrier at least 1 m thick with a hydraulic conductivity of 1.10^{-9} $m.s^{-1}$ is required for municipal waste landfills, as established in European Council Directive 1999/31/EC (OJEC, 1999). In the United States, the Environmental Protection Agency (EPA) imposes groundwater protection measures, although the owners/operators of Municipal Solid Waste landfills are given flexibility in the design of their units: for example, the ability to use a liner, and the type and thickness of the liner system may vary from state to state (EPA, 1993).

Due to the long-term storage of waste or the use of waste in construction materials, pollutants are either in contact with soils or transported through the ground when mixed with rainfall under varying temperature conditions. Hence, climatic pressure leads to pollutant leaching towards the soil. Depending on the soil mineral composition, and more specifically the clay proportion, this composition acts as an initial barrier for pollutant retention. Retention properties are indeed expected to depend on soil water content upon first contact with the soil. Beyond these potential soil retention properties, which must be determined through laboratory testing, the reversibility of pollutant fixation needs to be investigated as well. Consequently, the presence of various pollutant species, such as heavy metals, in soil constitutes a potential source of groundwater pollution. In the literature, some authors point out the fact that

renewable resources like groundwater must be preserved in the interest of human health and the important challenge this represents (Rosegrant, 1997).

The accumulation of toxic metals in soils, soil organisms, plants and groundwater can have a dramatic impact on water supply quality, which in turn may pose a health risk to human and animal populations (Brigatti et al., 1995). For example, despite being essential to life in low concentrations, copper at excessive levels may be detrimental to health. Heavy metal retention is thus the basic property required to introduce geochemical barriers against aquatic pollution. In this context, expansive compacted clays are often used as engineered barriers for household waste disposal sites; the typical retention properties of these barriers will now be investigated.

Over the past few decades, many studies have been conducted to demonstrate the role of expansive clay minerals in retaining pollutant metals and hence in limiting their mobility within natural systems; these studies have also been aimed at improving the understanding of sorption processes. On the one hand, experiments have been carried out to test the parameters controlling these processes, such as pH, ionic strength (e.g. Auboiroux et al., 1996; Abollino et al., 2003; Tan et al., 2008; Zhu et al., 2008) and the competitiveness of clay minerals (Helios Rybicka et al., 1995). While on the other hand, models have been developed to describe the primary mechanisms involved, i.e. cation exchange, surface complexation (e.g. Bradbury and Baeyens, 1997; Tournassat et al., 2004) from the micrometric down to the nanometric scale.

Cation Exchange Capacity (CEC) is a key parameter typically found in the literature for evaluating the retention properties of clays. CEC can be defined as the quantity of cations available for exchange at a given pH (Bergaya and Vayer, 1997) and has two origins: 1) the presence of permanent charges resulting from isomorphous substitutions in the octahedral and

tetrahedral sheets of clay minerals, and 2) the formation of negative charges at the edges (Ammann et al., 2005).

For this paper, laboratory tests are performed to characterise the soaking and retention properties of a clay barrier under controlled homogeneous conditions. A physical model that allows calculating the retention properties and kinetics observed during the test is then detailed, and lastly simulations are examined using various soaking conditions.

2. Experimental methods

2.1. Materials and solutions

The expansive mineral clay used in this investigation is a French clay known as Fo-Ca, which represents a natural Ca-smectite originating in the Paris basin from the Ypersian (Sparnacian) age. This Fo-Ca clay has been characterised during a previous study (Jullien et al., 2002) by inductively coupled plasma atomic emission spectrometry (ICP-AES) as well as by X-ray diffraction. The Cation Exchange Capacity (CEC) of Fo-Ca was determined by applying the cobalt complex method (Orsini and Rémy, 1976), for which 250 mg of dry clay were suspended in 25 mL of a 0.0167 M (i.e. 0.05 eq L^{-1}) cobaltihexamine solution ($[Co(NH_3)_6]Cl_3$), with a pH equal to 6.0. The samples were shaken for 2 hours and then centrifuged at 19,000 revolutions per minute for 1 hour. The Co concentration of each supernatant was measured by means of colorimetry using a Hitachi U-1100 spectrophotometer, at a wavelength of 473 nm. The CEC values were calculated as follows:

$$CEC = (C_i - C_f).(V / mc).10 \quad (1)$$

with CEC being expressed in meq/10 g of calcined clay, C_i is the initial concentration (eq L^{-1}), C_f the final concentration (eq L^{-1}), V the volume (L), and m_c the mass of clay (g) obtained

after calcination at 1,000°C for 12 hours. In opting for this procedure, the CEC of the Fo-Ca clay is equal to 8.0 ± 0.6 meq/10 g.

For the present study, pollutant retention is being investigated using a single ion; the copper ion was chosen in reference to numerical simulations (Wu and Li, 1998), which revealed the greater mobility of this ion in comparison with other heavy metals under the nearly neutral leachate. The soaking copper solutions were prepared by dissolving copper nitrate in distilled water. The copper concentration had to be made realistic by taking into account both the composition of landfill leachates and the laboratory test duration. The review by Christensen et al. (2001) showed that copper concentrations in landfill leachates are low, ranging from 0.005 to 10 mg L^{-1}, i.e. between 8.10^{-8} and 2.10^{-4} mol L^{-1}. The targeted concentrations were ultimately set equal to 0.1 mol L^{-1} (pH = 4.0) and 0.2 mol L^{-1} (pH = 3.1), according to a previous study (Jullien et al., 2002) and in order to minimise pollutant transfer time, hence the test duration. The chosen value of 0.1 mol L^{-1} has been overestimated compared to the concentrations measured in leachates at waste disposal sites, though it remains acceptable.

2.2. Laboratory test conditions

Specific equipment has been developed for this experimental campaign. The 40-mm diameter oedometric cell is composed of manganese bronze in order to obtain a low oxidising capacity relative to aggressive chemical solutions injected into the clay samples. Nitrates are not aggressive for oedometric cells (Fig. 1). The cell has been equipped with a piston for mechanical stress control. Axial displacements of the piston are then measured with a dial indicator accurate to within 0.5 µm. Porous sintered bronze plates surrounded by Teflon waterproof rings are used at both the top and bottom of the cell. Moreover, these porous plates are protected by filter paper to prevent pore obstruction by the clay.

The oedometer is connected to an injection system called a syringe (Jullien and Lecomte, 2000). Solute is injected by applying mechanical pressure to the solute, with a piston connected to a pressure control device, as shown in Fig. 1. Total syringe volume equals 500 mL and comprises materials that are inert with respect to a chemically-aggressive nitrate solution. If necessary, extra solution can easily be added into the syringe using a reservoir (Fig. 1). The volume of solute intake, measured from syringe piston displacements, is read from a dial indicator. Negligible strains on the syringe are obtained over the range of applied injection pressures, all of which lie below 1 MPa.

The solute injection pressure is thus separately controlled from the mechanical pressure applied to the clay sample.

A set of experiments was performed in order to assess long-term mass transfer under polluted conditions, through use of copper concentrations equal to 0.1 mol L^{-1} and 0.2 mol L^{-1}, which thus allows determining the behaviour of clay as a barrier. The solution was injected starting at initial saturation degrees (Sr = 0.3) to test the influence of the initial pollutant concentration on long-term clay barrier behaviour. In both cases, the final density of clay after compaction reached 1.2 kN m^{-3}.

For all tests, 5-mm high samples were prepared from 10 g of raw Fo-Ca powder placed inside the oedometer cell (Fig. 1), then compacted to 0.5 MPa and finally unloaded. Following this procedure, the initial gravimetric water content of samples equalled 12.5%. For the soaking step, the sample was reloaded using a constant solute injection pressure up to 0.3 MPa, applied at the upper boundary (syringe), while the lower boundary was subjected to a 0.3 MPa mechanical stress. Such test conditions led to a rather short liquid leaching duration at the non-injected sample boundary, as indicated during a previous study (Jullien et al., 2002). Both the solute intake and axial strain were monitored throughout testing for all samples, and their stability was verified as part of these experiments.

2.3. Experimental results

During the long-term experiments, leachates expelled from the clay were collected every 48 hours. The pH value was measured and concentrations of the Cu^{2+} metal pollutant, as well as Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, Fe^{2+} and the major clay cations, were analysed by means of Atomic Absorption Spectrometry (AAS) using a Hitachi Z-8100 spectrophotometer. A flame spectrometer was used to measure Cu concentrations ranging from 10^{-6} to 10^{-1} mol L^{-1}, and a graphite atomizer enabled the measurements of Cu concentrations from 8 10^{-8} mol L^{-1} to 10^{-6} mol L^{-1}. As previously demonstrated (Jullien et al., 2002), the measured instantaneous concentrations of cations could be accumulated to yield a new representation that allows deriving a conclusion regarding the ability of clay to fix copper and release cations over time. Fig. 2 shows the cumulative expelled copper during the experiment for a given initial copper concentration of the solution. Once the clay is saturated with copper, all input copper cations are expelled. The slope of the cumulative input vs. output concentration curves are then expected to be identical, as displayed in Fig. 3, with the delay required to reach such a regime denoted τ. Fig. 4 provides both the primary expelled cumulative cations (Ca^{2+}, Na^{+}) for the two initial copper concentrations and the total expelled cations (Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, Fe^{2+}). Though analysed separately by AAS, only the total expelled cations are considered for purposes of this model. The evolution over time of the total cation release has been modelled in order to quantify retention capacity. Fig. 4 also reveals the limitation of the exchange process in the form of an asymptote, corresponding to the CEC of the studied clay (which has been determined separately). The same phenomenon (i.e. asymptote for the exchange process) actually occurs with both 0.1 and 0.2 mol L^{-1} for the copper solute intake, although saturation of the clay with copper cations is reached after a shorter soaking time when solute concentration is higher.

3. Modelling details

3.1. General equations

The previously studied clay samples can be considered as a box subjected to a known external function x(t) that delivers a known response, expressed as y(t). Both x(t) and y(t) can be determined from the kinds of experimental results discussed above. The box is assimilated to its transfer function that links x(t) and y(t). The model of such a system containing both a box and x(t) and y(t) is based on the concept of dynamic systems with transient and static regimes. This type of time-dependent system may be described by a differential equation, e.g.:

$$b_m.\frac{d^m y}{dt^m} + ... + b_1.\frac{dy}{dt} + b_0 y = a_n.\frac{d^n x}{dt^n} + ... + a_1.\frac{dx}{dt} + a_0 x \qquad (2)$$

Such equations are usually solved using a Laplace transform. The transfer function H(s) of the system is thus obtained by a Laplace transform of Equation (1) for initial conditions set equal to zero, which then yields:

$$H(s) = \frac{Y(s)}{X(s)} = \frac{a_n s^n + ... + a_0}{b_m s^m + ... + b_0} \qquad (3)$$

where *s* is the Laplace variable.

Since the kinetics of cation exchange in the clay is a very slow phenomenon, the clay can be modelled by a first-order linear system, in which case the differential equation is reduced to:

$$\tau.\frac{dy}{dt} + y = H.x \tag{4}$$

where τ is the time constant, and H the gain for the permanent regime. H(s) can then be reduced to:

$$H(s) = \frac{Y(s)}{X(s)} = \frac{H}{1+\tau.s} \tag{5}$$

In knowing x(t), X(s) can be calculated by a Laplace transform of x(t); moreover, by using the Laplace table, y(t) can be deduced.

3.2. Modelling y(t), the cumulative copper concentration in leachate

The system response y(t) corresponding to the copper flux in leachate (see Arrow 3 in Fig. 1) is given by:

$$y(t) = BH\ (t - \tau + \tau e^{(-t/\tau)}) \tag{6}$$

Both B and τ need to be determined, while H equals 1. In this case, B is derived from x(t), which represents the copper solute intake (meq) under permanent hydraulic test conditions (i.e. a constant soaking rate). x(t) is expressed by Equation 7 below:

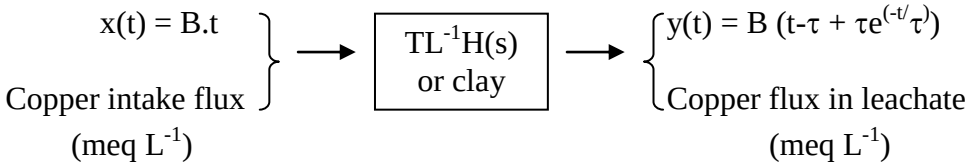
$$x(t) = B.t \tag{7}$$

B is then calculated by applying the following equation:

$$B = V.C \tag{8}$$

where V is the solute injection rate in mL h^{-1} (Fig. 1) and C the copper intake concentration, expressed in eq L^{-1}.

Under fixed soaking pressure conditions, the permanent regime is reached when the pollutant flux intake is identical to the expelled flux. The H parameter given in (5) becomes equal to 1. All these modelling hypotheses can be summarised into a global system, as depicted below:



(9)

where τ is known as the time constant.

4. Experimental results

To analyse model robustness and validate the approach, these experimental results were first compared to simulations derived from modelling the aforementioned 0.1 and 0.2 mol L^{-1} copper injection tests. The model time constants could then be calculated, i.e. τ for the expelled copper measurements. These constants are then determined for each experimental copper intake concentration and fitted along with several other injected copper concentrations, as depicted in Fig. 5.

Fig. 6 presents for both tests (i.e. 0.1 and 0.2 mol L^{-1} copper injection) a set of comparisons between cumulative copper concentration changes vs. time in leachates. Fig. 7 shows model predictions of cumulative cation concentrations in leachates (i.e. copper retention by clay). These curves are accurately fit by the model with the experimental data for the leaching phenomena. Further simulations were subsequently conducted and will be discussed below.

5. Discussion

The model proposed in this paper is, according to the above results, considered as a possible means for investigating the exchange/retention properties of clay as a barrier over a wider range of copper injection concentrations. The trends observed when using this model under such circumstances will be discussed below.

The simulations of cumulative copper concentration in leachate will lead off this discussion. The predictions for initial copper concentrations varied between 0.05 and 0.5 mol L^{-1} and are displayed in Fig. 7. This curve shows the kinetic variations with concentrations as well as the expected gradient for a wide range of pollutant concentrations relative to potential landfill conditions.

Fig. 8 illustrates the model predictions of cumulative cation concentrations in leachates, as given in meq/L, for initial experimental copper concentrations together with the experimental results. All the data fit well with the model. Fig. 9 shows only the model predictions of cumulative cation concentrations in leachates, as given in meq L^{-1}, for initial experimental copper concentrations ranging between 0.05 and 0.5 mol L^{-1}. All cumulative concentrations in meq L^{-1} are then bound by CEC, as was introduced into the model. These curves show that the model offers a description of exchange kinetics as well.

It can be stated at the end of this discussion that beyond the fact that the model exhibits an accurate prediction of experimental laboratory test findings for the expelled cumulative copper, this prediction is also valuable in terms of expelled cations. Furthermore, clay retention capacity until reaching a physical limit in the exchanges is evidenced as well, with this limit being input into the model as the clay CEC.

6. Conclusion

A physically-based model for both clay leaching, when injected with copper pollutants of various concentrations, and clay retention capacity has been proposed in this paper. Model principles have relied on the cation exchange properties of clay, as limited by the clay CEC value. The results from both model runs and experiments for two copper solute concentrations prove that the model can indeed predict experimental results with a good level of accuracy. The model was then applied to simulating a range of copper input concentrations compatible with ranges found in landfill site data.

The hypothesis adopted, which considers the clay sample as a system subjected to an external load (such as a polluted solution) and delivering a response to this load, leads to a simple model that enables simulating and predicting the evolution of both copper and exchangeable cation concentrations in leachates over time. The model's physical basis using the clay CEC easily allows for adaptation to other expansive clays, since just the CEC value needs to be determined, whereas only two tests have to be performed to determine leaching properties. Moreover, the simulations performed as part of this study have yielded good predictions of the phenomena observed on oedometric laboratory soaking paths for small compacted clay samples introducing copper solutions. They have also provided an effective means for predicting pollutant transfer through clay barriers, whose transfer lasts a very long time.

This model offers the opportunity to predict saturation times for more dilute copper concentrations, once the time constant has been determined. Both the framework and methods can then be improved with further investigations performed on other pollutants.

Acknowledgements

The authors gratefully thank Patrick Lecomte for his technical assistance.

References

Abollino, O., Aceto, M., Malandrino., M., Sarzanini, C., Mentasti, E., 2003. Adsorption of heavy metals on Na-montmorillonite. Effects of pH and organic substances. Water Research 37, 1619-1627.

Ammann, L., Bergaya, F., Lagaly, G., 2005. Determination of the cation exchange capacity of clays with copper complexes revisited. Clay Minerals 40, 441-453.

Auboiroux, M., Baillif, P., Touray, J.C., Bergaya, F., 1996. Fixation of Zn^{2+} and Pb^{2+} by a Ca-montmorillonite in brines and dilute solutions: Preliminary results. Applied Clay Science 11, 117-126.

Bergaya, F., Vayer, M., 1997. CEC of clays: Measurement by adsorption of a copper ethylenediamine complex. Applied Clay Science 12, 275-280.

Bradbury, M.H., Baeyens, B., 1997. A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part II: modelling. Journal of Contaminant Hydrology 27, 223-248.

Brigatti, M.F., Corradini, F., Franchini, G.C., Mazzoni, S., Medici, L., Poppi, L., 1995. Interaction between montmorillonite and pollutants from industrial waste-waters: exchange of Zn^{2+} and Pb^{2+} from aqueous solutions. Applied Clay Science 9, 383-395.

Christensen, T. H., Kjeldsen, P., Bjerg, P. L., Jensen, D. L., Christensen, J. B., Baun, A., Albrechtsen, H.-J., Heron, G., 2001. Biogeochemistry of landfill leachate plumes. Applied Geochemistry 16, 659-718.

EPA, 1993. Criteria for solid waste disposal facilities. A guide for owners/operators. United States Environmental Protection Agency, EPA/530-SW-91-089, pp. 1-20.

Helios Rybicka, E., Calmano, W., Breeger, A., 1995. Heavy metals sorption/desorption on competing clay minerals; an experimental study. Applied Clay Science 9, 369-381.

Jullien, A., Lecomte, P., 2000. Dispositif perméamétrique à injecteur à pression contrôlée séparé. Brevet Français N°00/07820.

Jullien, A., Proust, C., Le Forestier, L., Baillif, P., 2002. Hydro-chemio-mechanical coupling effects on permeability and swelling behaviour of a Ca smectite soaked by Cu solutions. Applied Clay Science 21, 143-153.

OECD, 1997. Recycling strategies for road works, Organisation for Economic Co-operation and Development OECD (Ed.), Paris, France.

OJEC, 1999. Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste. Official Journal of the European Communities, L 182, pp. 1-19.

Orsini, L., Rémy, J.C., 1976. Utilisation du chlorure de cobaltihexamine pour la détermination simultanée de la capacité d'échange et des bases échangeables des sols. Sciences du Sol 4, 269-275.

Rosegrant, M.W., 1997. Water resources in the twenty-first century: challenges and implications for action, in: International Food and Policy Research Institute (Eds), Food, Agriculture, and the Environment Discussion, Paper 20, Washington D.C., pp. 1-26.

Tan, X.L., Chang, P.P., Fan, Q.H., Zhou, X., Yu, S.M., Wu, W.S., Wang, X.K., 2008. Sorption of Pb(II) on Na-rectorite: Effects of pH, ionic strength, temperature, soil humic acid and fulvic acid. Colloids and Surfaces A: Physicochemical and Engineering Aspects 328, 8-14.

Tournassat, C., Ferrage, E., Poinsignon, C., Charlet, L., 2004. The titration of clay minerals. II. Structure-based model and implications for clay reactivity. Journal of Colloid and Interface Science 273, 234-246.

Wu, G., Li, L.Y., 1998. Modeling of heavy metal migration in sand/bentonite and the leachate pH effect. Journal of Contaminant Hydrology 33, 313-336.

Zhu, S., Hou, H., Xue, Y., 2008. Kinetic and isothermal studies of lead ion adsorption onto bentonite. Applied Clay Science 40, 171-178.

Figure 1. The experimental equipment: (1) nitrate copper solute intake, (2) clay sample, (3) leachate

Figure 2. Concentration influence on leachate kinetics

Figure 3. Cumulative cation concentrations measured in leachates versus time

Figure 4. Copper cumulative concentration in leachates- experiments and simulations for the two injected copper concentrations : 0.1 and 0.2 mol/L.

Figure 5. Exchangeable cations in leachate(Na^{+}, Ca^{2+}, Mg^{2+})- experiments and simulations for the two initial copper concentrations equal to 0.1 and 0.2 mol/L versus time.

Figure 6. Evolution of the time constant for the models versus copper concentration of the injected copper concentration.

Figure 7. : model predictions of copper concentration in the leachate for various injection concentrations.

Figure8. : model predictions and experimental results of copper cumulative concentration in the leachate for various injection concentrations.

Figure 9 : model predictions of cation concentration in the leachate for various injection concentrations.

Figure 1.

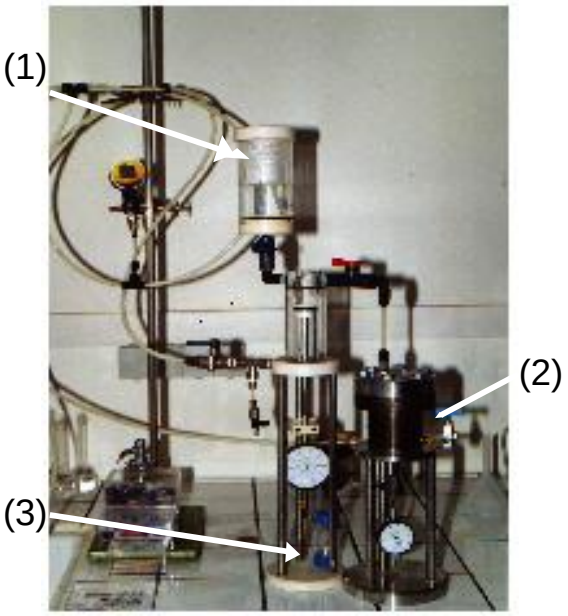


Figure 2

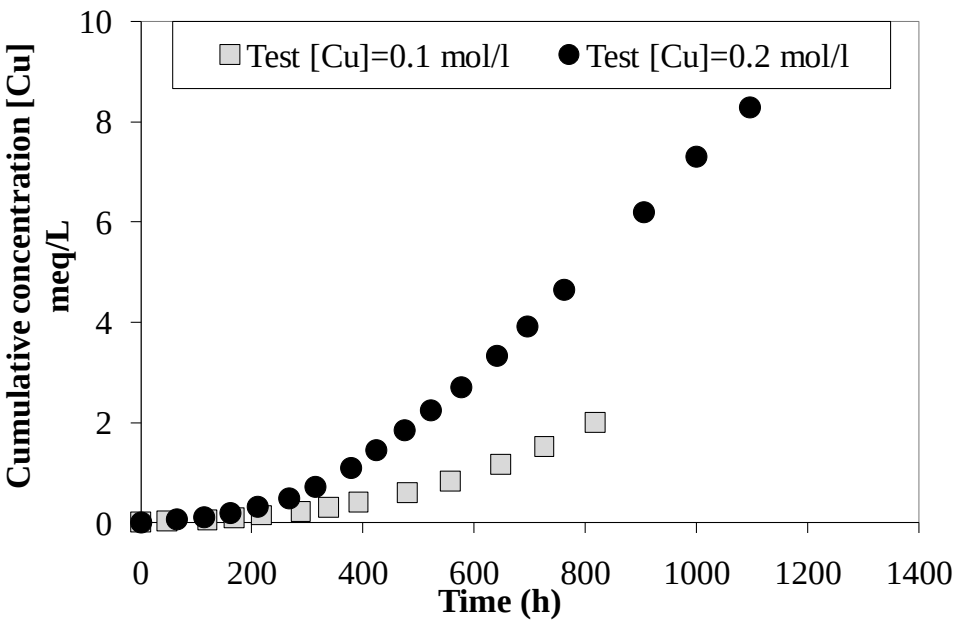


Figure 3

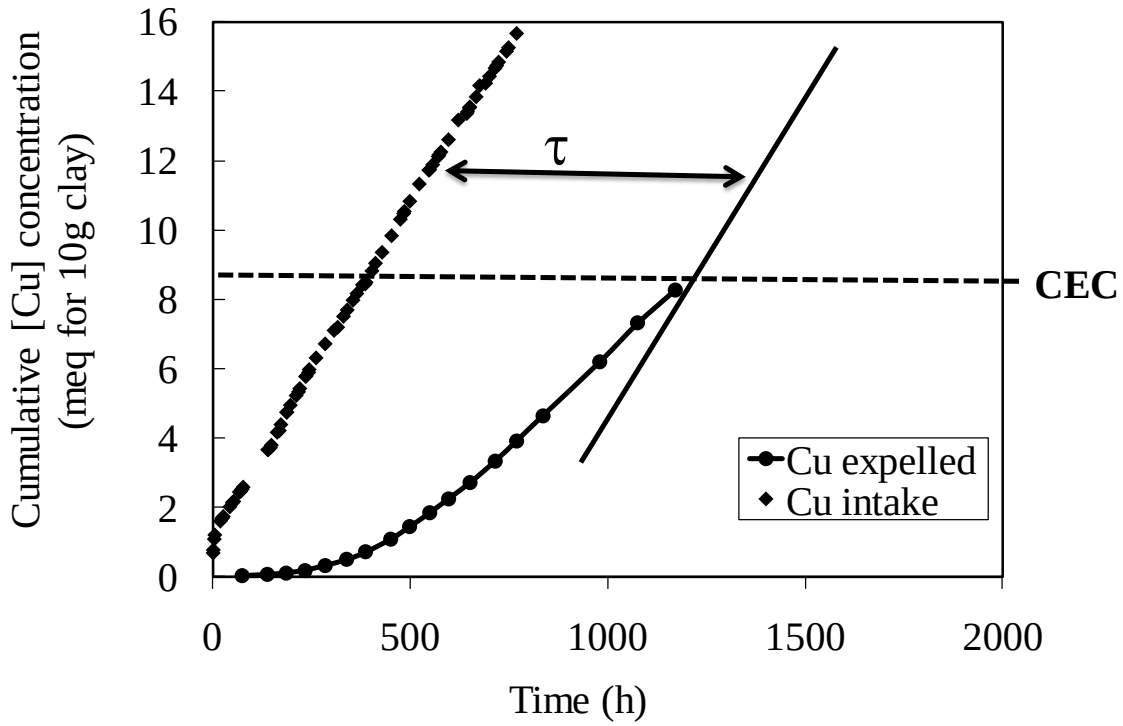
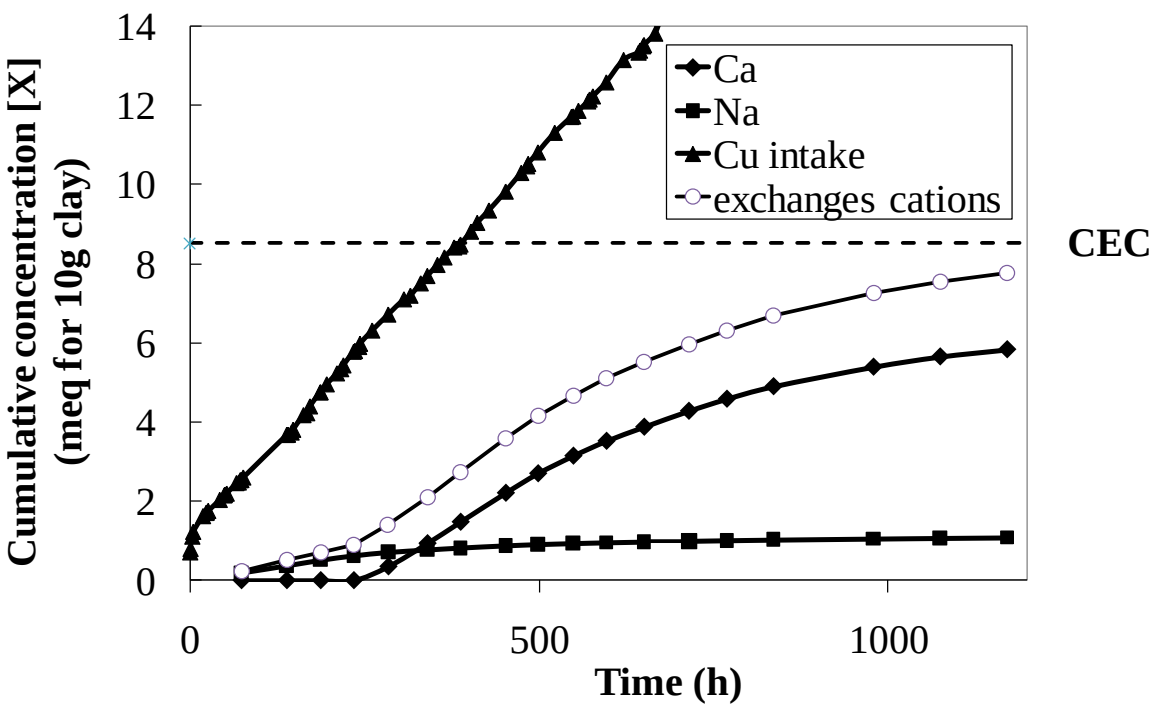


Figure 4



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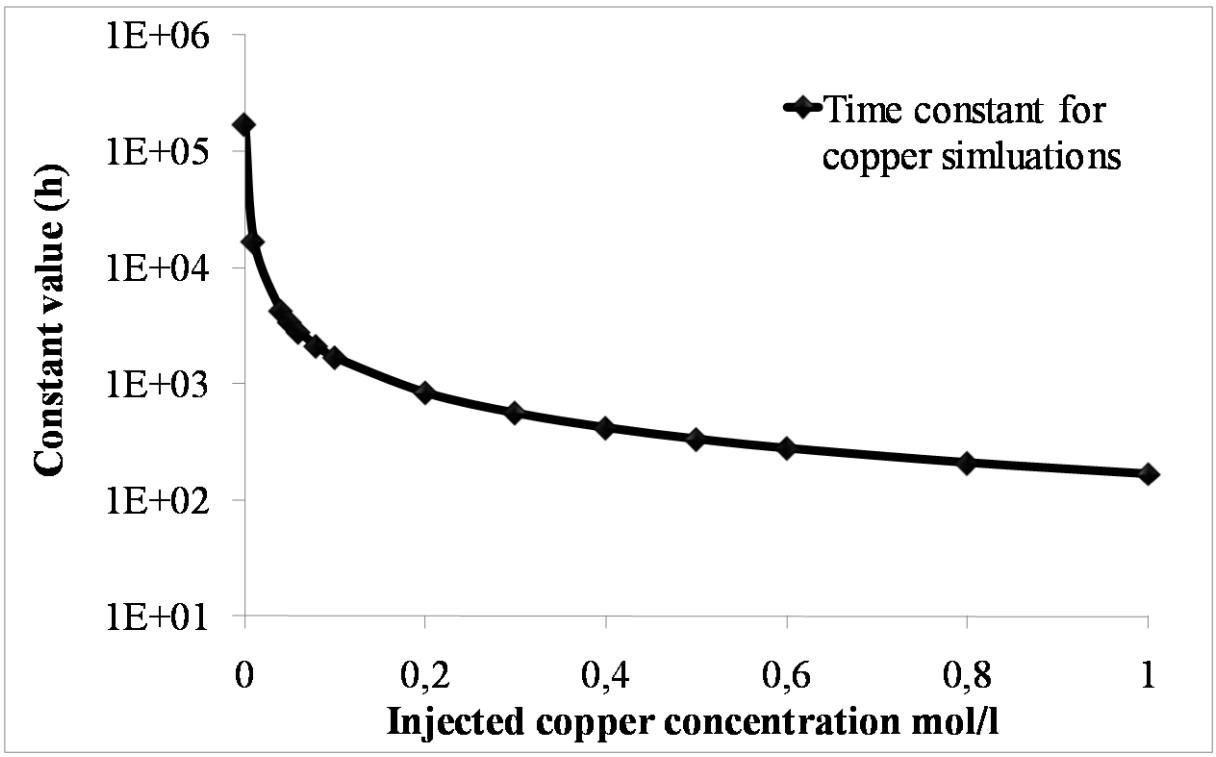

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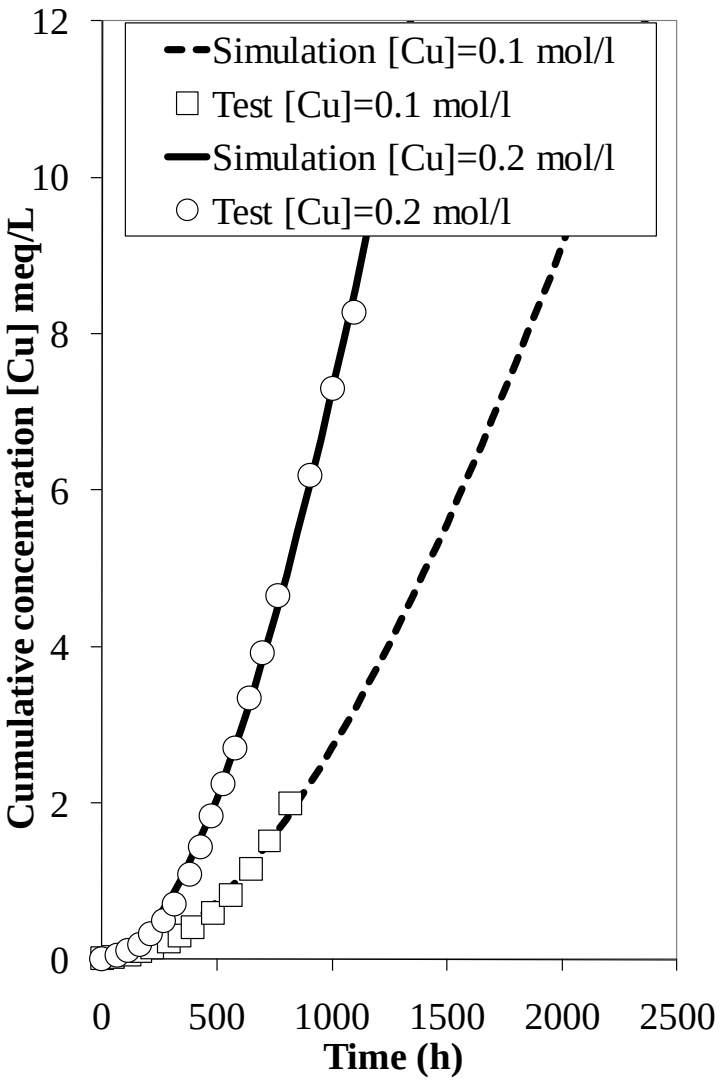
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Test [Cu]=0.1 mol/l
Simulation [Cu]=0.2 mol/l
Test [Cu]=0.2 mol/l
Cumulative concentration [Cu] meq/L
Time (h)
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10
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1000
1500
2000
2500

Figure 7.

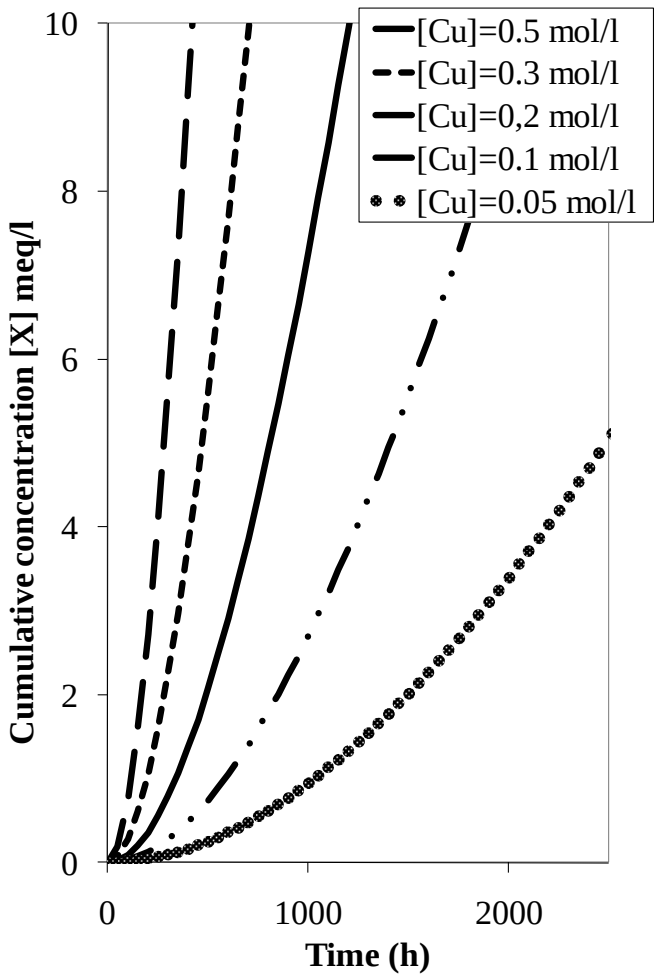
[Cu]=0.5 mol/l
[Cu]=0.3 mol/l
[Cu]=0,2 mol/l
[Cu]=0.1 mol/l
[Cu]=0.05 mol/l
Cumulative concentration [X] meq/l
Time (h)
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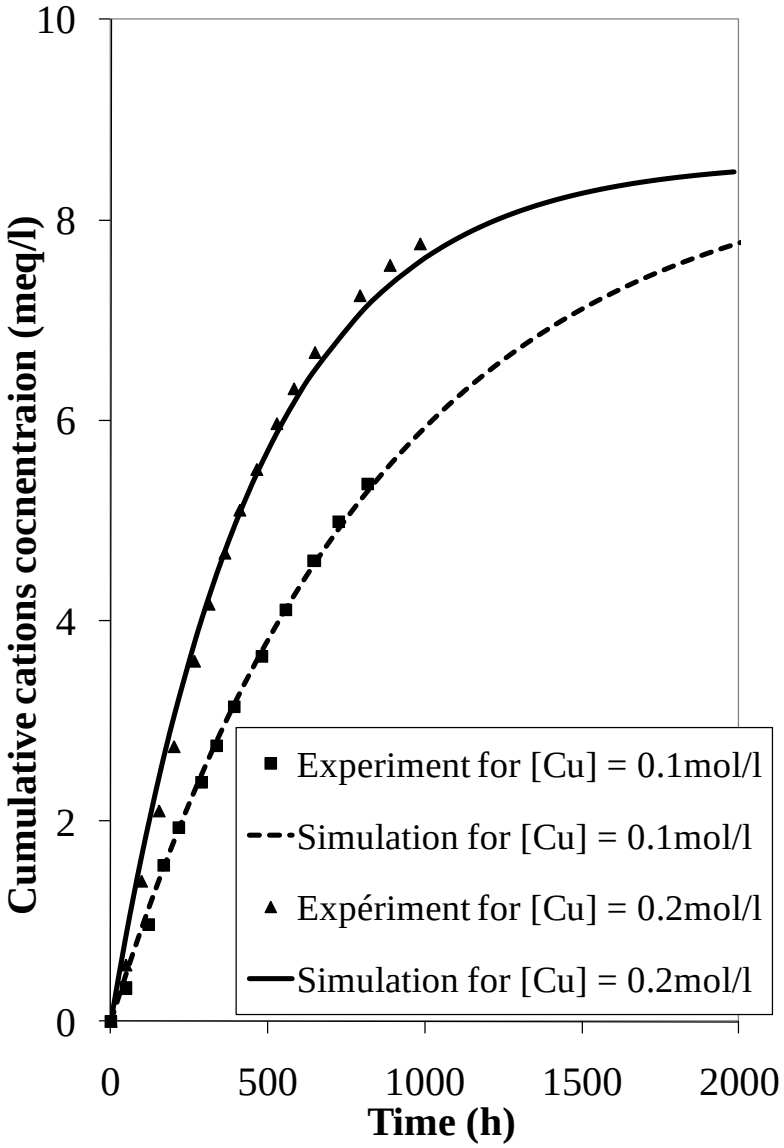
Fig 8.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Cumulative cations cocnentraion (meq/l)
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Experiment for [Cu] = 0.1mol/l
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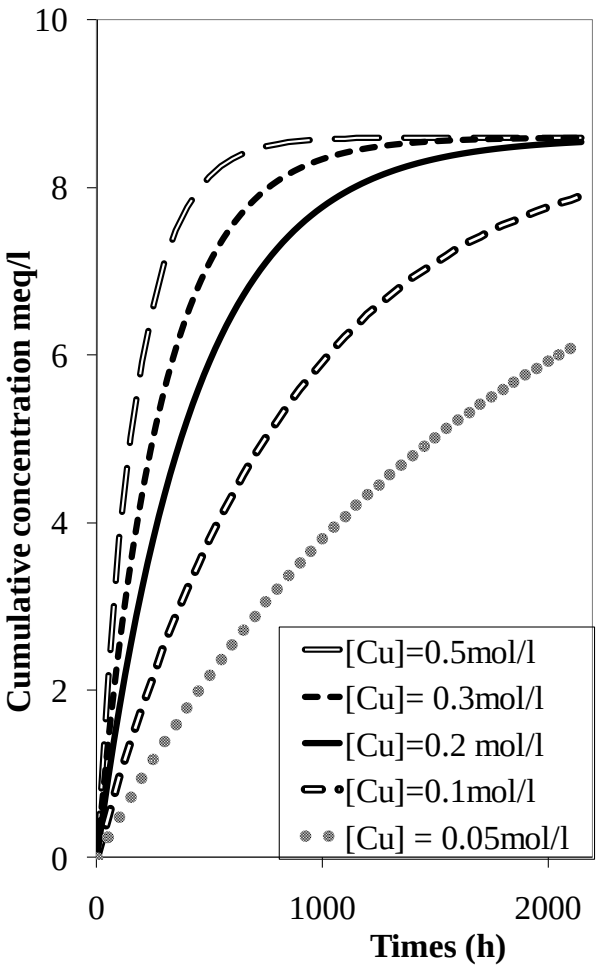
Simulation for [Cu] = 0.2mol/l

Figure 9 :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Cumulative concentration meq/l
Times (h)
[Cu]=0.5mol/l
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[Cu]=0.2 mol/l
[Cu]=0.1mol/l
[Cu] = 0.05mol/l